

PATENT SPECIFICATION

(11)

1 455 701

1 455 701

(21) Application No. 18958/73 (22) Filed 19 April 1973
 (23) Complete Specification filed 3 April 1974
 (44) Complete Specification published 17 Nov. 1976
 (51) INT. CL.² C08J 3/18
 C08G 18/12
 C08L 27/06 //
 B32B 27/04 27/22 27/30 5/26 7/10
 (C08L 27/06 87/00)

(52) Index at acceptance
 C3P 10D1A E2 PC13A PC20D1 PC20D3 PC8B S2
 B5N 0526 0710 2704 2722 2730
 C3R 7C 7J C12 C25 L2X
 (72) Inventors ROWLAND GIBSON
 PETER RICHMOND GRINDLEY
 DOROTHY JOYCE GUEST



(19)

(54) POLYVINYL CHLORIDE PLASTISOL COMPOSITIONS

(71) We IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to plasticisers and 10 more particularly to plasticiser compositions for use with polyvinyl chloride.

Polyvinyl chloride (PVC) is used in plasticised form in the manufacture of extruded and moulded articles and sheet, for the coating of fabrics and for many other applications. Plasticised PVC may be fabricated from plastisols, which are very finely divided unplasticised PVC dispersed, together with stabilisers, in a plasticiser to form a creamy 15 paste. The dispersion remains spreadable and free-flowing and the polymer in it remains unplasticised until the temperature is raised. At 80-110°C the dispersion sets to a 20 low strength product, but when the temperature is raised above 150-160°C it becomes plasticised and workable so that it can be fabricated into useful articles. This method is widely used and has the advantages that 25 no solvents need be used, and the initially 30 fluid paste can be deposited where required and gelled *in situ*.

The plasticisers which are used as described above are generally high boiling esters of, for example, phthalic, phosphoric 35 or sebacic acids with C₁₂-C₁₈ alcohols, and various fatty acid derivatives. Polymeric plasticisers are also used, for example, polyesters derived from adipic, sebacic or azelaic acid with a glycol, for example, 40 propylene glycol or butylene glycol.

The most commonly used plasticisers are the phthalic esters, for example, dibutyl phthalate, dioctyl phthalate, di-(2-ethylhexyl) phthalate, diisooctyl phthalate and the di- 45 ester of phthalic acid with C₁₂-C₁₈ alcohols

(‘diaphenyl phthalate’), trixylyl phosphate, dioctyl adipate or sebacate, polypropylene and polybutylene segacates, adipates and azelates and epoxidised soya bean oil. The phosphate esters provide some degree of fire 50 retardance. Alkyl diesters of sebacic and adipic acids are low temperature plasticisers. Polyester plasticisers offer especially good performance.

It is known to add isocyanates to the dispersion of PVC in a plasticiser as a bonding agent in order to improve the adhesion of the plasticised PVC, obtained by heating the dispersion at an elevated temperature, to the substrate to which it is applied. This 55 improved adhesion is particularly valuable when PVC coated synthetic fabrics for example, nylon or polyester fabrics, are to be manufactured. Especially good results are obtained by the use of isocyanurate polymers of organic polyisocyanates, which are generally prepared by polymerising the organic poly-isocyanate, for example, tolylene diisocyanate in solution in a suitable solvent, in the presence of a catalyst. The solvents 60 used are usually low boiling esters, for example, ethyl acetate or butyl acetate.

The addition of a solution of the polymerised diisocyanate in a low boiling solvent as mentioned above has certain disadvantages. Thus, local precipitation of the isocyanurate polymer may occur on addition of its solution to the PVC plastisol, the viscosity of the plastisol is disturbed, the volatile solvent is driven off when the plastisol 80 is heated and causes bubbles in the mixture, and the solvent is usually highly inflammable and its escape into the atmosphere is objectionable for this reason and also because of its odour and the increasing consciousness of potential ecological hazards.

These disadvantages are largely overcome by the present invention, which provides polyvinyl chloride plastisol compositions containing an isocyanurate polymer of an 85 90

organic polyisocyanate wherein the isocyanurate polymer has been added to the plastisol as a solution in a solvent which is an effective plasticiser for polyvinyl chloride.

5 The invention also provides a process for the manufacture of the isocyanurate polymer solutions and includes the use of the above-defined plastisol compositions as adhesives and for the coating of textiles and other substrates, and the substrates so coated.

10 It is preferred but by no means essential that the solvent which is used for preparing the solution of the isocyanurate polymer is the same as the plasticiser used in preparing the plastisol. Preferred solvents are those esters of phthalic and sebacic acids and polyesters of adipic, sebacic and azelaic acids already mentioned above as being suitable plasticisers for PVC.

15 The isocyanurate polymer is preferably derived from tolylene diisocyanate and more particularly from the commercially available mixtures of the 2,4- and 2,6- isomers thereof in the proportions 80:20 or 65:35 by weight. However, other polyisocyanates may also be used to prepare the isocyanurate polymer, for example, *p*-phenylene diisocyanate, 1-methoxyphenylene-2,4-diisocyanate, 3,3-dimethyl-4,4'-diisocyanatodiphenylmethane, diphenylene-4,4'-diisocyanate, 4,4'-diisocyanatodiphenyl ether, naphthylene-1,5-diisocyanate, hexamethylene diisocyanate, diisocyanatodicyclohexylmethane, *p*-xylylene diisocyanate, isocyanatobenzyl isocyanates, 1, 2, 3, 4, 5, 6-hexahydrodiphenylene-4,4'-diisocyanate, 4,4'-diisocyanato-1, 2, 3, 4, 5, 6-hexahydrodiphenylmethane, 1, 2, 3, 4-tetrahydronaphthylene-1,5-diisocyanate, toluene-2, 4, 6-triisocyanate, 3-methyl-4, 6, 40 4'-triisocyanato diphenylmethane, 2, 4, 4'-triisocyanatodiphenyl, 2, 4, 4'-triisocyanatodiphenyl ether and, particularly, 4,4'-diisocyanatodiphenyl methane, *m*-phenylene diisocyanate, 1-chlorophenylene-2,4-diisocyanate, *m*-xylylene diisocyanate and *p*-isocyanato benzyl isocyanate.

45 Mixtures of isocyanates may be polymerised. Organic polyisocyanates may be polymerised with aromatic mono-isocyanates, for example, phenyl isocyanate, tolyl isocyanates, chlorophenyl isocyanates or methoxyphenyl isocyanates.

50 The solution of the isocyanurate polymer is added to the plastisol to provide preferably from 1 to 15% by weight, of isocyanurate based on the weight of PVC.

55 The isocyanurate polymer solution is prepared by polymerising the organic poly-isocyanate in solution in a solvent which is an effective plasticiser for polyvinyl chloride, in the presence of an isocyanate trimerisation catalyst, the catalyst being subsequently removed or de-activated when trimerisation has proceeded to the desired extent. The

60 solvent is one of those esters or polyesters already defined above as being suitable plasticisers for PVC. The reaction is preferably carried out at an elevated temperature, temperatures in the range 100-150°C being particularly suitable.

65 Suitable isocyanate trimerisation catalysts include basic catalysts such as tertiary amines, basic metallic compounds such as alkali metal or alkaline earth metal oxides, hydroxides, carbonates, alcoholates or phenates and alkali metal salts of weak organic acids. Co-catalysts may be used, for example, alcohols, phenols, mono-N-substituted carbamic esters or cyclic oxides.

70 Examples of specific suitable catalysts are sodium methoxide, potassium hydroxide, sodium acetate, potassium acetate, sodium and potassium carbonate, sodium phenate, sodium octylphenate, sodioacetoacetic ester, sodium stearate, sodium 2-ethylhexoate, lead 2-ethylhexoate, calcium octoate, lead laurate, zinc naphthenate, lead naphthenate, cobalt naphthenate and manganese linoleate.

75 The amount of catalyst required depends upon the activity of the catalyst and the nature of the polyisocyanate. Amounts within the range 0.01 to 10% by weight of the polyisocyanate are generally found useful; in the case of catalysts of high activity, about 0.1% to 1.0% is suitable.

80 When the requisite degree of polymerisation has been achieved, further polymerisation may be prevented, for example, by mechanical removal of insoluble catalyst by filtration of the catalyst. If the catalyst is in solution, it may be rendered inactive by treating the product with the calculated amount, or a slight excess, of a strong acid, for example, anhydrous hydrogen chloride, sulphuric acid or phosphoric acid. Any 85 inactive insoluble material so produced may be removed by filtration.

85 According to a further feature of the invention there is provided a method for the coating of substrates with plasticised polyvinyl chloride which comprises applying to the substrate a polyvinyl chloride plastisol composition containing an isocyanurate polymer of an organic polisocyanate, as hereinbefore described, and heating the 90 plastisol-coated substrate to a temperature at which the polyvinyl chloride becomes plasticised. This temperature may be in the range 150 to 210°C, preferably 160-175°C. If desired the unplasticised coating on the 95 substrate may first be semi-gelled by heating to a temperature in the range 95 to 115°C, preferably 100-110°C, before raising the temperature to the level at which the polyvinyl chloride becomes plasticised.

100 This semi-gelling stage is particularly desirable when more than one coat of plastisol is to be applied to a substrate, each coat being semi-gelled before application of the next, otherwise adhesion between the 105

110

115

120

125

130

coats may not be satisfactory.

According to yet a further feature of the invention there is provided a method for the manufacture of laminated or bonded articles which comprises applying to the surfaces of the materials which are to be bonded together a polyvinyl chloride composition containing an isocyanurate polymer of an organic polyisocyanate, as hereinbefore described, placing the coated surface of the materials in contact and applying pressure at a temperature sufficient to cause the polyvinyl chloride to become plasticised, i.e. 150-120°C, preferably 160-175°C.

Again, the plastisol coatings may be semi-gelled by heating to 95 to 115°C, preferably 100 to 110°C before placing the coated surfaces in contact and subjecting the materials to pressure and heat at the final plasticising temperature.

On cooling, a strong bond between the two materials forming the laminate is obtained. The materials which are bonded together may be the same or different, and the process can be extended to the bonding together of more than two layers of materials to form a multiple-ply laminated article.

Both the coating and laminating processes are particularly applicable to fabric substrates, and it is possible to apply a polyvinyl chloride coating to, for example, polyester film by the use of this process.

The invention is illustrated but not limited by the following Example in which parts and percentages are by weight.

Example

(a) Preparation of an isocyanurate polymer of tolylene diisocyanate in diethyl phthalate as solvent.

100 parts of a 65/35 mixture of 2,4-/2,6-tolylene diisocyanate are dissolved in 300 parts of diethyl phthalate having a water

content of not greater than 0.03% and an acid value corresponding to <0.1 mg KOH/g. Using a calcium octoate catalyst system, 45 activated with *tert*-butyl phenol and under an atmosphere of pure dry nitrogen, the tolylene diisocyanate is trimerised at 120°C until the isocyanate content of the mixture is in the range 3.6 to 3.8%.

When the reaction has proceeded to the desired level, the catalyst is de-activated by the addition of orthophosphoric acid.

The product is a clear, pale straw coloured solution having a viscosity of approximately 35 poises at 25°C. A similar product may be prepared by replacing diethyl phthalate with dibutyl phthalate.

(b) Incorporation of the isocyanurate solution (a) into PVC plastisols.

The PVC plastisols described in the Table below were prepared by the following method. The PVC polymer was stirred with the stabiliser and 40 parts of the plasticiser for 5 minutes in a dough mixer. The remainder of the plasticiser was added and stirring was continued a further 5 minutes. The plastisol was then allowed to stand for 1 hour and the bonding agent, where used, was stirred in slowly with minimum entrainment of air. Viscosity of the plastisol was measured at intervals using a Ferranti-Brookfield viscometer.

A square-woven twistless nylon textile fabric was coated with the plastisols by spreading with a hand doctor blade. The coatings were semi-gelled in an air oven at 110°C. Two plies of coated fabric were placed with their coated faces in contact and fused and laminated in a press at 175°C 80 under light pressure. The bond strength of the laminate was measured by peeling apart a 1-inch wide strip on an Instron (Registered Trade Mark) tensile testing machine.

85 *Table*

Mixes A and B are included for comparative purposes only.

		A	B	C
90	PVC paste-grade polymer (Corvic P65/54) ("Corvic" is a Registered Trade Mark)	100	100	100
95	Di-2-ethylhexylphthalate ("DOP")	65	65	54*
	Stabiliser (Basic lead carbonate paste)	5	5	5
	Isocyanurate bonding agent as 40% solution in butyl acetate as solvent (prepared as described below)	—	10**	—
100	Isocyanate bonding agent in PVC plasticiser according to (a) above	—	—	15**
	Bond strength (kilogrammes/inch width)	1.5	6.0	7.5
	Pot life of Plastisol (room temperature, hours)	>1 week	12	20
	Plastisol Viscosity (Brookfield)	30 min.	38,000	8,000 37,200
	(Time measured from addition of bonding agent in cases of mixes B and C)	60 min.	38,200	8,100 37,600
	Odour of gelled test specimen	120 min.	38,000	10,800 36,200
			Slight, No solvent	Marked solvent odour
			odour.	odour.

105 * Dosage adjusted to allow for the DOP content of the bonding agent.

** Dosages chosen to give approximately equal isocyanate values.

The butyl acetate solution of isocyanurate polymer used in the above Examples was prepared as follows:—

100 Parts of a 65/35 mixture of 2,4,2,6-tolylene diisocyanate are dissolved in 150 parts of butyl acetate having a water content of <0.05% and an acid value corresponding to <0.1 mg KOH/g. Using a calcium octoate catalyst system activated by 5 *tert*-butylphenol and under an atmosphere of pure dry nitrogen, the tolylene diisocyanate is trimerised at 60-70°C until the isocyanate content of the mixture is in the range 5.7-6.1%.

15 When the reaction has proceeded to the desired level, the catalyst is de-activated by the addition of orthophosphoric acid.

The results in Table 1 demonstrate that 20 the isocyanurate bonding agent gave a technologically satisfactory improvement of bond to the textile compared with Mix A; gave improved pot life compared with Mix B; gave a markedly less reduced viscosity when the bonding agent was added as compared 25 with Mix B; and avoided the solvent odour associated for a considerable time after production with fabrics coated with Mix B. The freedom from solvent odour and solvent fumes associated with Mix C also provides 30 a much improved working environment during the operations of mixing and coating, and greatly diminishes the risk of atmospheric pollution arising from both these operations and from the gelation procedure.

35 **WHAT WE CLAIM IS:—**

1. Polyvinyl chloride plastisol compositions containing an isocyanurate polymer of an organic polyisocyanate wherein the isocyanurate polymer has been added to the plastisol as a solution in a solvent which is an effective plasticiser for polyvinyl chloride.

2. Compositions as claimed in claim 1 wherein the solvent for the isocyanurate 45 polymer is the same as the plasticiser used in preparing the plastisol.

3. Compositions as claimed in claim 1 or claim 2 wherein the solvent for the isocyanurate polymer is an ester of phthalic, phosphoric or sebacic acid with a C₁-C₁₂ alcohol or a polyester derived from adipic, sebacic or azelaic acid and a glycol.

4. Compositions as claimed in any one of claims 1 to 3 wherein the isocyanurate polymer is derived from tolylene diisocyanate.

5. Compositions as claimed in any one of claims 1 to 4 wherein the solution of the isocyanurate polymer is added to the plastisol to provide from 1 to 15% by weight of 55 isocyanurate polymer based on the weight of polyvinyl chloride.

6. Polyvinyl chloride plastisol compositions as claimed in claim 1 and substantially as hereinbefore described with reference to the foregoing Example.

7. A process for the preparation of a solution of an isocyanurate polymer of an organic polyisocyanate in a solvent which is an effective plasticiser for polyvinyl chloride which comprises polymerising the organic polyisocyanate in solution in the solvent, in the presence of an isocyanate trimerisation catalyst, the catalyst being removed or deactivated when trimerisation has proceeded to the desired extent.

8. A process as claimed in claim 7 wherein the solvent is an ester of phthalic, phosphoric or sebacic acid with a C₁-C₁₂ alcohol or a polyester derived from adipic, sebacic or azelaic acid and a glycol.

9. A process as claimed in claim 7 or claim 8 wherein the trimerisation reaction is carried out at a temperature from 100 to 150°C.

10. A process as claimed in any one of claims 7 to 9 wherein the trimerisation catalyst is a tertiary amine, an alkali metal or alkaline earth metal oxide, hydroxide, carbonate, alcoholate or phenate or an alkali metal salt of a weak organic acid.

11. A process as claimed in any one of claims 7 to 10 wherein the trimerisation catalyst is used together with a co-catalyst.

12. A process as claimed in claim 11 wherein the co-catalyst is an alcohol, a 95 phenol, a mono-N-substituted carbamic ester or a cyclic oxide.

13. A process as claimed in any one of claims 7 to 12 wherein the amount of catalyst used is from 0.01 to 10% by weight, 100 based on the weight of the organic polyisocyanate.

14. A process as claimed in claim 13 wherein the amount of catalyst is from 0.1 to 1.0% by weight.

15. A process as claimed in any one of claims 7 to 14 wherein the catalyst is deactivated by treating the product with a strong acid.

16. A process for the preparation of a 110 solution of an isocyanurate polymer of an organic polyisocyanate in a solvent which is an effective plasticiser for polyvinyl chloride, substantially as hereinbefore described with reference to the foregoing Example.

17. A solution of an isocyanurate polymer of an organic polyisocyanate in a solvent which is an effective plasticiser for polyvinyl chloride, whenever obtained by a process 120 as claimed in any one of claims 7 to 16.

18. A method for the coating of substrates with plasticised polyvinyl chloride which comprises applying to the substrate a polyvinyl chloride plastisol composition as 125 claimed in claim 1 and heating the plastisol-coated substrate to a temperature at which the polyvinyl chloride becomes plasticised.

19. A method for the manufacture of laminated or bonded articles which com- 130

prises applying to the surfaces of the materials which are to be bonded together a polyvinyl chloride plastisol composition as claimed in claim 1, placing the plastisol-
5 coated surfaces in contact and applying pressure at a temperature sufficient to cause the polyvinyl chloride to become plasticised.

20. A method as claimed in claim 18 or claim 19 wherein the plasticising temperature is in the range 150-210°C.

21. A method as claimed in claim 20 wherein the plasticising temperature is 160 to 175°C.

22. A method as claimed in any one of claims 18 to 21 wherein the plastisol coating is semi-gelled before placing the coated surfaces in contact by heating to a temperature in the range 95 to 115°C before raising the temperature to the level at which the polyvinyl chloride becomes plasticised. 20

23. A method as claimed in claim 22 wherein the semi-gelling temperature is 100 to 110°C.

24. A method for the manufacture of laminated or bonded articles substantially 25 as hereinbefore described, with reference to the foregoing Example.

25. Laminated or bonded articles whenever obtained by a method as claimed in any one of claims 19 to 24. 30

26. Substrates coated with plasticised polyvinyl chloride whenever obtained by a method as claimed in any one of claims 18 and 20 to 23.

D. VINCENT,
Agent for the Applicants.

Printed for Her Majesty's Stationery Office by The Tweeddale Press Ltd., Berwick-upon-Tweed, 1976.
Published at the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.